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(54) **Time-of-flight Mass Spectrometer**

(57) In a time-of-flight mass spectrometer ions of different masses and energies are emitted by a source 12. The flight path of the ions to a collector 20 is folded by arranging for multiple reflections of the ions by a plurality of ion mirrors R1, R2...RN. The mirrors are such that the ion flight time is independent of the ion energy. Preferably ions of different energies are allowed to bunch.

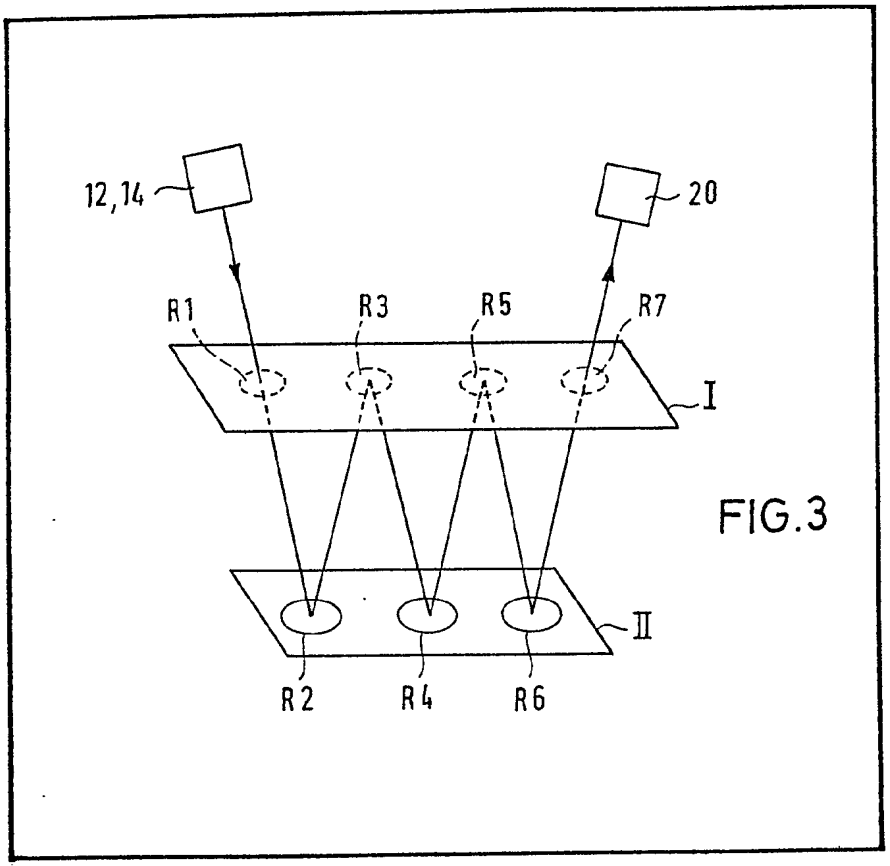

FIG.3

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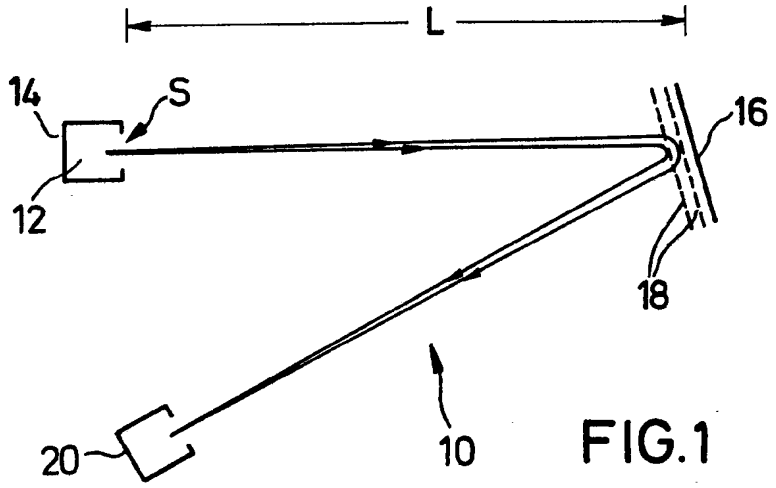

FIG.1

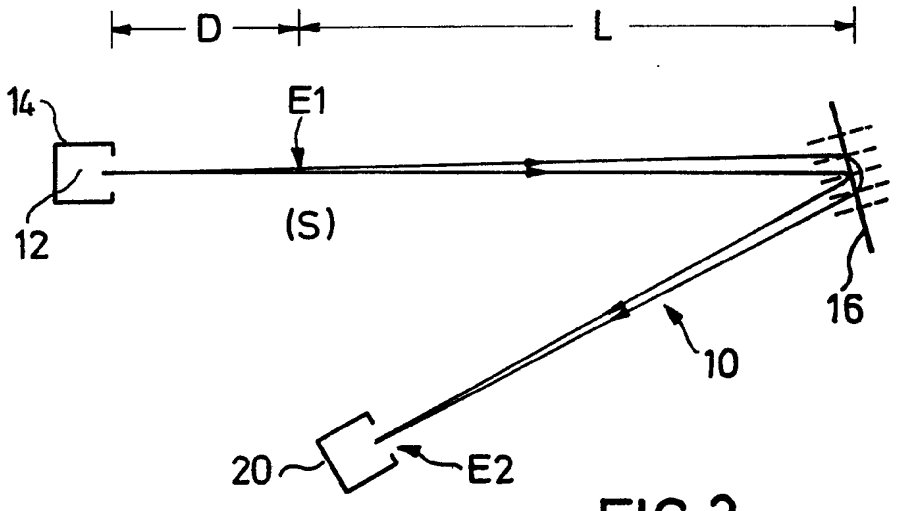

FIG.2

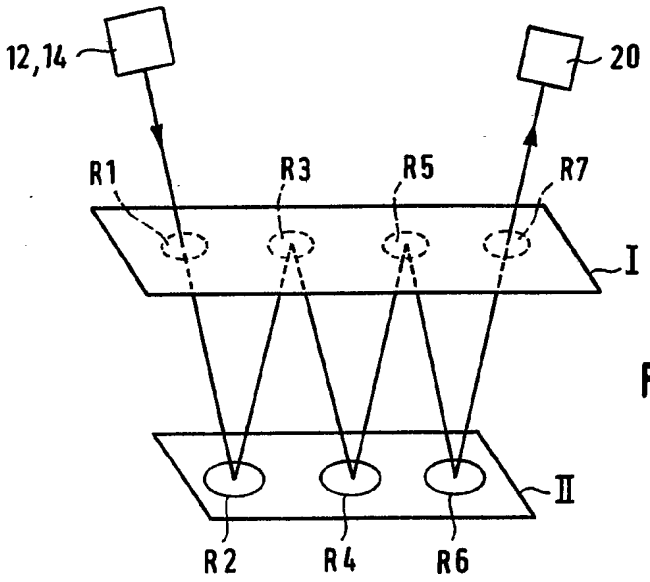
12,14
20
R1
R3
R5
R7
I
II
R2
R4
R6

FIG.3

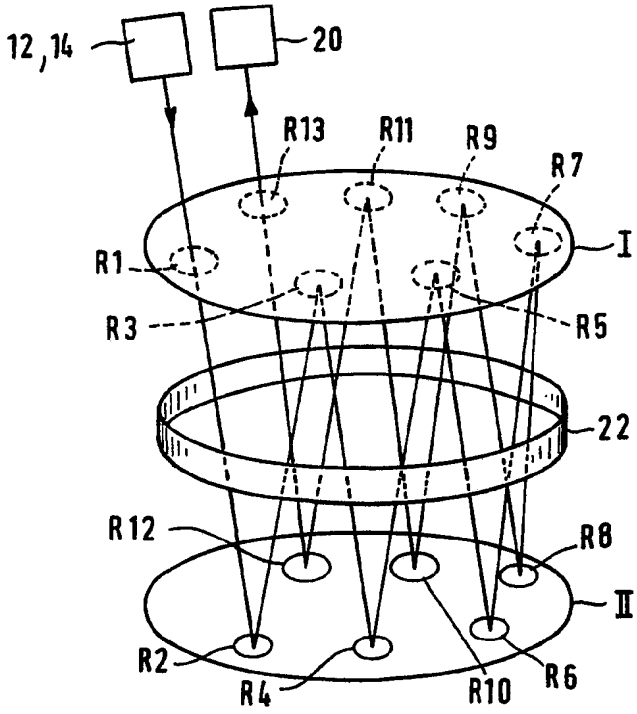
12,14
20
R13
R11
R9
R7
I
R1
R3
R5
22
R12
R8
II
R2
R4
R10
R6

FIG.4

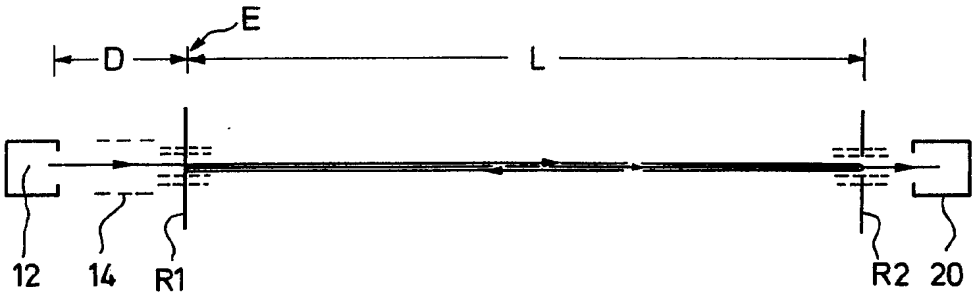

FIG. 5

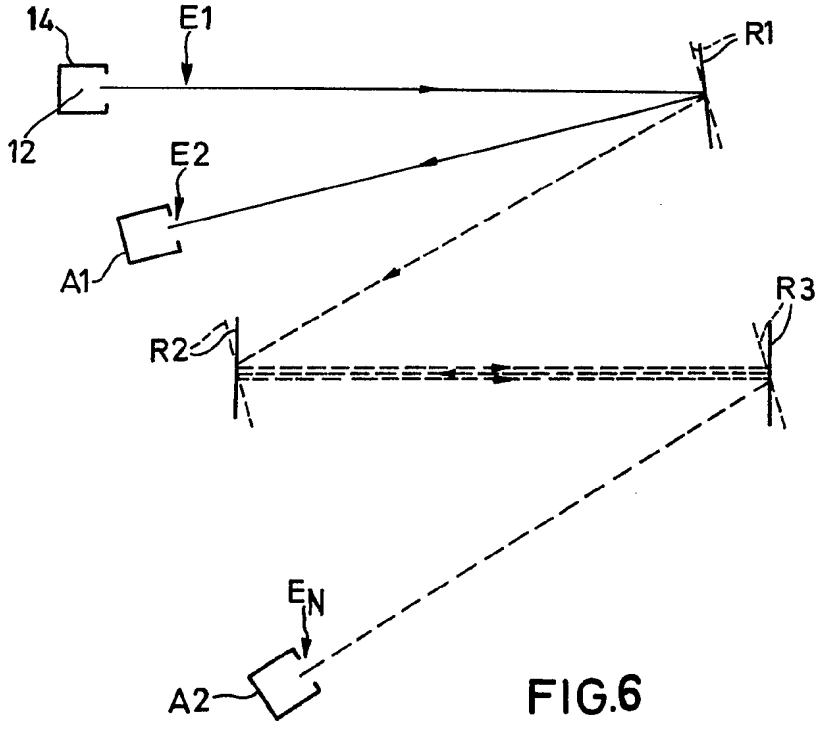

FIG.6

SPECIFICATION

Time-of-flight Mass Spectrometer

The present invention relates to a time-of-flight mass spectrometer.

In time-of-flight mass spectrometers ions of the same energy but of different mass are separated from one another if they traverse the same path lengths with different velocities and arrive successively at an ion collector or secondary electron multiplier. In this connection it is important that all ions start at the same time at the beginning of their flight path.

A special arrangement for a time-of-flight mass spectrometer (Fig. 1) has been proposed in Soviet Patent Specification 198 034, cf. BA. Mamyrin et al Zh. Tekh. Fiz. 41 (1971), 1498—Sov. Phys.-Tech. Phys. 16 (1972), 1177, in which the ion energy need no longer be the same for all ions. After the ions have traversed a path length (L) they are deflected by almost 180° by an electrostatic mirror so that they have to travel back along the said path before they can be recorded in an ion secondary electron multiplier arrange directly adjacent to the ion source. In this connection it is essential that ions of somewhat higher energy penetrate deeper into the ion mirror composed of grid plates; overall, they therefore have to traverse a longer path than ions of somewhat lower energy. By means of a suitable potential distribution in the ion mirror, it could be arranged that the flight time of the ions from the source to the secondary electron multiplier depends only on the ion mass and not on the ion energy, though with the drawback of considerable ion current losses.

Since the mass resolution in a time-of-flight mass spectrometer is proportional to the length of the flight path, it is desirable to make the latter large. Even when using an ion mirror or Mamyrin's type, i.e. with a double utilisation of the structural length, this involves an extensive and bulky system in which in addition the diameters of the ion collectors and ion mirrors must be large. It is true that the ion collector at least can be reduced in size by introducing focusing elements such as individual electrostatic lenses, but the diameter of the ion mirror still remains large.

The object of the invention is to provide an improved flight mass spectrometer subject to reduced ion current losses, and to achieve, with a simplified, space-saving construction, an increased resolving power.

This objective is achieved in accordance with the invention by a time-of-flight mass spectrometer comprising an ion source for emitting ions of different masses and energies, an ion collector and means including a plurality of ion mirrors defining a flight for ions between the source and the ion collector, the ion mirrors being arranged and controlled to provide multiple reflections of the ions along a folded path and so that the ion flight time is independent of the ion energy.

The particular feature of the time-of-flight mass spectrometer according to the invention is the multiple reflections of the ions within the flight path; this repeated folding or bending of the flight path is equivalent to the sequential arrangement of a plurality of (simple) time-of-flight mass spectrometers together with their ion mirrors. For relatively little expenditure on apparatus and equipment, the ion flight path is thus extended and hence the resolution of the whole system is improved for the same ion pulse length. By using a number N of such ion mirrors (with 100% reflection) the structural length can thus be utilised not only twice, but (N+1) times. In this connection, the number N of ion mirrors may either be odd or even.

In a time-of-flight mass spectrometer the mass resolution increases on the one hand if the ion pulse length is reduced. On the other hand however the ion intensity falls with decreasing ion pulse length. A high mass resolution can be combined with a high intensity by providing a further path section of length D between the ion source and the start E of the flight path as seen by the ion mirrors instead of using, as in a time-of-flight mass spectrometer according to Mamyrin et al, a directly connected, pulsed ion source. At the beginning of an ion pulse the source can thus emit ions of low energy, and then ions of increasingly higher energy and thus greater velocity. By suitably dimensioning and controlling the apparatus, the quicker ions will have caught up with the slower ions, which started earlier, in each case at the point E. A substantially shorter ion pulse is thus produced at this point without any ion current loss, and in addition the energy width of the pulse has increased. In particle accelerator technology this procedure is called ion bunching.

The pulse length at the catching up point E is D. ΔU, where ΔU is the unavoidable energy width with which the ions left the source at a specific point in time. In order to make the pulse length at the catching up point E as short as possible, D will thus be chosen as small as possible; in certain cases, e.g. if the ion production is restricted to a brief moment, this catching up effect can be disregarded completely, and in these cases D is thus chosen equal to zero.

In a time-of-flight mass spectrometer of the type illustrated in Figs. 1 and 2 of the drawings, the ion beam diameter increases with the ion flight path. In order to counteract this, a focusing lens can be introduced into the beam path, which reduces the beam diameter at the site of the ion collector.

It is further very advantageous to use the ion mirror itself as the focusing element. In this case it is not constructed, as is usual, of parallel metal nets forming in each case a specific potential surface; instead, it comprises a series of apertures, tubes or the like which are at different potentials. Similar to a Möllenstedt filter lens operating in a transmission mode, such as ion mirror operating in a reflection mode provides focusing effects which can be computed.

Furthermore, ion beam losses, which are unavoidable in the passage of an ion beam through conventional nets, are obviated with ion mirrors of focusing apertures.

The invention will now be further described with reference to the accompanying schematic drawings, in which:

Fig. 1 is a diagrammatic view of a time-of-flight mass spectrometer according to the prior art,

Fig. 2 is a similar view of part only of a time-of-flight mass spectrometer according to the invention,

Fig. 3 is a diagrammatic oblique view of an embodiment of a time-of-flight mass spectrometer according to the invention, comprising a planar linear arrangement,

Fig. 4 is an oblique view of another embodiment of a time-of-flight mass spectrometer according to the invention, comprising a circular cylindrical arrangement,

Fig. 5 illustrates the principle of a further embodiment of a time-of-flight mass spectrometer according to the invention, with controllable ion mirrors, and

Fig. 6 illustrates the principle of yet another embodiment of a time-of-flight mass spectrometer according to the invention with electrostatically tiltable ion mirrors.

The time-of-flight mass spectrometer 10 illustrated in Fig. 1 corresponds to the literature citation mentioned at the beginning (Mamyrin et al) and comprises, as shown diagrammatically, an ion source 12 as well as a deflecting device 14 for the ion beam which is bent at an ion mirror 16 by grid plates 18 and is directed to an ion collector (a secondary electron multiplier) 20. Ions of different energies leave the starting point S and travel the length L of the mass spectrometer before reflection at the mirror 16.

Parts of a time-of-flight mass spectrometer according to the invention resemble this arrangement superficially, as can be seen from Fig. 2, and identical elements are thus identified by the same reference numerals. Thus shown also in Fig. 2 is an ion source 12 with a deflecting device 14 for an ion beam, which is deflected at the ion mirror 16 and directed to a collector 20. However, the dimensioning and regulation involved is considerable if ions of higher energy that started later are to catch up or "bunch" at a first catching up point E1 with other ions of the same mass but of lower energy which started on their path earlier. The ion mirror 16 composed of apertures, tubes or the like (not shown) has in addition a focusing effect so that "bunched" ions meet at a second catching up point E2 at the ion collector 20. This arrangement ensures, thanks to the extra section D (between the ion source 14 and the first catching up point E1), that the total flight time on the adjoining section L depends only on the ion mass and not on the ion energy, with the result that minimally short ion pulses are produced at the collector. By regulating the potential distributions in a sequential arrangement of N ion mirrors 16 and a different penetration depth of the ions in the mirrors is in each case achieved according to the invention. Figs. 3 and 4 show two examples of embodiments comprising N mirrors 16 (here designated R1, R2 etc.) arranged in two planes I and II. A catching up point E2, E3, etc., is thus created in this way after each mirror R1, R2, etc. It can even be arranged that the first catching up point after that located at the distance D behind the ion source 14, is situated at the ion collector 20.

It is convenient and envisaged (though not illustrated) to use focusing elements or focusing ion mirrors with sequential arrangements of N ion-mirrors. The smallest possible mirror and lens diameters can be used if the focal lengths of the mirrors R1, R2, etc., and of the lenses are all equal to 1/2, L denoting the distance between two opposite mirrors. By means of extraction optics for the ion source 14 or an auxiliary lens, an image of the ion source 14 can be produced at the point of the beam reversal in the first mirror R2 of the plane II (Figs. 4 and 5), whereas there is an aperture diaphragm at the site of the beam reversal in the first mirror R1 of plane I, just as is required in the case of annular accelerators in order to produce good beam adaptation in the centre of the focusing element.

The ion mirrors R1, R2, etc, for deflecting the beam may be arranged adjacent to one another on a straight line in a plane (Fig. 3), or on a circle around a cylinder (Fig. 4). In general, each 1st mirror must be so tilted or tiltable, which can be carried out electrostatically or electromagnetically under electronic control, that the ion beam is deflected onto the centre of the following (1+1)th mirror.

In the case of Fig. 3 this means that the mirrors in the first two planes I and II are in each case arranged linearly and parallel so that the ion beam is reflected backwards and forwards in a transverse plane until it exits at the last ion mirror (R7) and reaches an ion collector arranged therebehind. In the embodiment of Fig. 4 the individual ion mirrors R1, R2, etc., are arranged in each case on a circle in each of the two planes I, II, with the result that the corresponding enveloping surface can be a cylinder or also a cone. A substantially parallel arrangement of all the ion mirrors is also possible in this case by interposing an electrode 22 which deflects the ion beam at each passage roughly in the direction of the centre of the whole arrangement.

It can be seen that the arrangements according to Figs. 3 and 4 utilise their structural length (L) N+1 times as an ion flight path, with the assistance of N ion mirrors. The invention also however provides the possibility of being able to cause the ion beam to oscillate N times between two ion mirrors R1 and R2 (Fig. 5). However, measures should be taken in this connection to channel the ion packet into this section ($\approx$L) between the two mirrors R1 and R2, as well as finally to deflect it again.

In the embodiment shown in Fig. 5 the ion

mirror potentials may be pulsed by suitable regulating means, instead of being kept constant. For example, the ion cloud may find the mirror R1 first of all earthed, i.e. not existing per se, whereas mirror R2 reflects the ions. The ion cloud returning from the mirror R2 is then reflected by the interposed mirror R1. After the ions have traversed the section between the mirrors R1 and R2, N times the electronic regulation provides that the ions at the (N+1)th approach to the mirror R2 will find the latter earthed, i.e. as non-existent per se. The ions may thus exit and reach the ion secondary electron multiplier 20.

In the embodiment shown in Fig. 6 mirrors R1, R2, etc. that can be tilted electronically for short periods are used, and the potential distribution is regulated for a short period in such a way that the ion beam is reflected at a different angle than previously; a moderately highly resolved time-of-flight mass spectrum can be recorded in the first collector (secondary ion multiplier) A1. If the mirror R1 is tilted for a short time, the ion beam passes to the mirror R2. This stays tilted in such a way during the passage of the ion cloud that it deflects the ion beam onto the mirror R3; the mirror R2 then tilts back and the ion cloud is reflected N times backwards and forwards between the mirrors R2 and R3 until, by briefly swivelling the mirror R3, the ion beam is deflected onto the second collector A2. A small range of ion masses that had been filtered out from the mass spectrum recorded in the first collector A1 is thus recorded with a high mass resolution in the collector A2.

Such beam tilting can also be carried out according to the invention by additional (not illustrated) tilting elements, e.g. electrostatic or magnetic devices.

Claims

1. A time-of-flight mass spectrometer comprising an ion source for emitting ions of different masses and energies, an ion collector and means including a plurality of ion mirrors defining a flight for ions between the source and the ion collector, the ion mirrors being arranged and controlled to provide multiple reflections of the ions along a folded path and so that the ion flight time is independent of the ion energy.

2. A mass spectrometer according to claim, wherein the potential distribution, the dimensioning and control of the ion mirrors is such that they see the start of the flight path as a point in front of the ion source whereat ions of lower energy produced earlier are caught up by ions of the same mass but higher energy that started later.

3. A mass sepctrometer according to claim 1 or 2, wherein the ion mirrors include apertures, tubes or the like, which can be charged at different electrostatic potentials.

4. A mass spectrometer according to claim 3, wherein those apertures, tubes or the like which are no longer reached or can scarcely still be reached by reflected ions are closed by grids.

5. A mass spectrometer according to any one of claims 1 to 4, which has such a mirror geometry and mirror potentials that in addition to the ion reflection the ions are focused at the collector.

6. A mass spectrometer according to any one of claims 1 to 5, wherein the flight path section lengths between two successive ion mirrors are in each case the same, or groups of ion mirrors with in each case equal interspacings are provided, and the focal lengths of the individual mirrors are exactly half as large as the mirror interspacings.

7. A mass spectrometer according to claim 6, wherein the required focal length is achieved by interposing individual lenses in front of the ion mirrors.

8. A mass spectrometer according to any one of claims 1 to 7, wherein a regulating system with time varying electrostatic or magnetic fields is provided in order to channel and deflect the ions which multiply traverse a section containing two or more ion mirrors.

9. A mass spectrometer according to claim 8, wherein a regulating arrangement with additional, pulsed, locally bounded electrostatic or magnetic deflecting fields is provided to channel and deflect the ions.

10. A mass spectrometer according to claim 8 or 9, wherein the regulating means for channeling and deflecting the ions includes a device for switching on and off the potentials of one or more of the ion mirrors, and the or each mirror allows the incident ions to pass through during the switch-off time.

11. A mass spectrometer according to any one of claims 8 to 10, wherein the regulating means for channeling and deflecting the ions includes a device for altering the reflection angle of one or more of the ion mirrors for a short time by means of time varying potentials.

12. A mass spectrometer according to any one of claims 1 to 11, wherein the ion mirrors comprise near spherical equipotential surfaces.

13. A mass spectrometer according to any one of claims 1 to 12, wherein the ion mirrors are arranged opposite one another in two planes.

14. A mass spectrometer according to claim 13, wherein the ion mirrors in each plane are arranged linearly in a plane running transverse thereto.

15. A mass spectrometer according to claim 13, wherein the ion mirrors of each plane are arranged on a circle.

16. A mass spectrometer according to any one of claims 13 to 15, including at least one deflecting electrode provided between the oppositely arranged ion mirrors in the two planes.

17. A time-of-flight mass spectrometer substantially as hereinbefore described with reference to figures 2 to 5 of the accompanying drawings.

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